A New Spectrophotometric Determination of Titanium with Sodium Alizarinsulfonate

A New Spectrophotometric Determination of Titanium with Sodium Alizarinsulfonate*

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Synopsis

It was found that alizarinsulfonate and stannous chloride were reduced by titanium in hydrochloric acid solution and turned to green, and using this reaction, a new method for the determination of very small amount of titanium by photometry was proposed. This new method is very sensitive and not affected by usual diverse ions, and very excellent one particulary in the point that it is not necessary to separate completely from other elements.

I. Introduction

There are several methods for the determination of titanium by photometry such as with hydroquinone,(1) chromotropic acid,(2) hydrogen peroxide(3) and so on. Both methods with hydroquinone and chromotropic acid, however, are so complicated that only the method with hydrogen peroxide is used practically for the analysis of iron, steel and other metals. But the peroxide method is not so sensitive, and it is necessary to separate the titanium from other elements, especially from vanadium and molybdenum completely. Szarvas et al.(4) reported that when the alizarinsulfonate in hydrochloric acid solution was reduced with hydrogen of nascent state by the addition of zinc, the solution turned to green by the catalytic action of titanium. The present authors found that by using sodium alizarinsulfonate and stannous chloride in hydrochloric acid solution, the color of the solution turned to green with the presence of titanium, and that this reaction could be applied to the photometric determination of titanium.

In the present experiments this reaction was fundamentally examined, so that the sensitive method for the photometric determination of small amount of titanium might be established. Moreover, the determination of small amount of titanium in iron, steel and other metals will be reported successiviely by applying this method.

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* The 880th report of the Research Institute for Iron, Steel and Other Metals. Published in the Jaural of the Chemical Society of Japan. **78** (1957), 373.

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II. Experiments and results

1. Reagents and apparatus

(i) Reagents

Hydrochloric acid: 12N and 6N of hydrochloric acid were used.

Ammonium oxalate solution: Saturated aqueous solution was used.

Sodium alizarinsulfonate: 0.2 per cent aqueous solution of sodium alizarinsulfonate was used. (A. S. will be used as the abbreviated expression in the following.)

Stannous chloride: 20 per cent hydrochloric acid (6N) solution was used.

Titanium standard solution: After 0.1624 g of analytical grade titanium oxide was fused with potassium hydrogen sulfate, the melt was dissolved in sulfuric acid solution and it was diluted to 200 ml. The concentration of this solution was determined volumetrically with liquid zinc amalgam method and the definite amount of this Standard Stock Solution was taken for every experiment and diluted exactly by 1N sulfuric acid and the titanium concentration was adjusted to be about 50 γ/1 ml.

(ii) Apparatus

Hitachi's photoelectric spectrophotometer EPU-2 type with 10 mm cell was used.

2. Experimental procedure

Take definite amount of the standard titanium solution and hydrochloric acid. Add the ammonium oxalate solution, the A. S. solution and the stannous chloride solution and then adjust the total volume to 10 ml by diluting with water. Allow to stand this mixed solution at room temperature for definite time and then measure to absorbance.

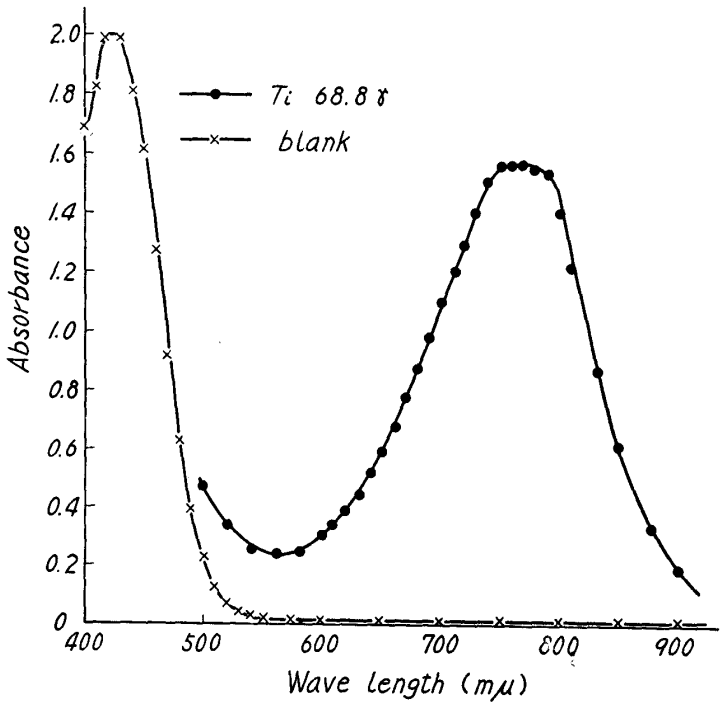

Fig. 1. Absorption Curve.

3. Absorption curve

68.8 γ of titanium, 4 ml of the hydrochloric acid, 2ml of the ammonium oxalate solution and 2 ml of the stannous chloride solution were mixed, which was diluted to 10 ml with water, hydrochloric acid concentration of this solution was 6N and its absorbance was measured by using water as reference. The absorption curve obtained in shown in Fig. 1. As seen in Fig. 1, the maximum absorbance occurred at the wave length

420~430 mμ in the case of blank solution and at 740~790 mμ in the case of the solution containing titanium. For the absorbance of blank solution it was negligibly small at 740~790 mμ, in which the photometry of titanium was most convenient. The absorbance at 760 mμ was used for the following experiments.

4. Kinds of acid and their concentrations

By preliminary experiments, it was found that the absorbance and the time required to get the maximum absorbance depended upon the concentration of hydrochloric acid. In the 10 ml solution containing always 57.4 γ of titanium, 2 ml of the ammonium oxalate solution, 0.7 ml of the A. S. solution and 2 ml of the stannous chloride solution, the concentration of hydrochloric acid was changed and the absorbance was estimated at the wave length 760 mμ. The relations between the time and the absorbance were obtained as shown in Fig. 2. As shown in Fig. 2, the velocity of the development of the coloration was very slow in the dilute hydrochloric acid, that is, the increase of the absorbance was small even after 45 minutes and the absorbance was still small. But the constant absorbance was obtained after 40 minutes in the 5N solution and after 25 min in the 6N solution. The absorbance was kept constant for 60 min and then gradually decreased. The reaction velocity of the coloration was very rapid in the 7.2 N solution, but the decoloration was also remarkably rapid, as the decoloration began already after 15 min. As mentioned above, the reaction velocity was very slow and the absorbance was also small, when the acid concentration was too small. On the other hand, at the 7N acid concentration the velocity of the coloration was rapid, but the decoloration velocity was also too rapid. Therefore, both cases were unsuitable for the photometry and about 6N of hydrochloric acid solution seemed to be suitable for the following experiments.

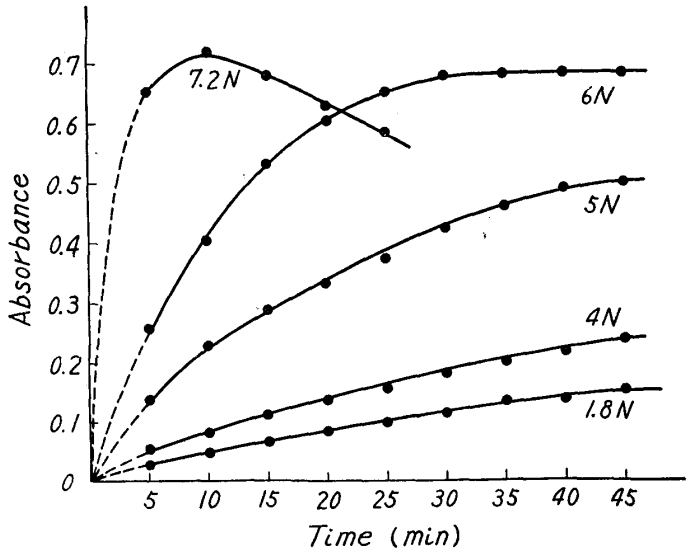

Fig. 2. The ralations between absorbance and time after mixed.

The more detailed experiments were carried out at around 6N solution with the solution containing 20.1 γ of titanium and with 5N, 5.5N, 6N, and 6.5N of the hydrochloric acid. The results obtained are shown in Table 1. It will be seen in Table 1 that the absorbance of the 6N solution was maximum and, accordingly, it is the most suitable concentration. Instead of hydrochloric acid, sulfuric acid or perchloric acid was also used. Because hydrochloric acid was not used, the stannous chloride solution was used after being dissolved in 6N sulfuric acid or 6N perchloric acid. 20.1 γ of titanium was taken, 4 ml of 12N sulfuric acid or

12N perchloric acid was added and the others were mixed exactly the same as mentioned above. The coloration was scarcely seen. Also the velocity of the coloration was very slow and the absorbance was very small, when only 6N hydrochloric acid solution of stannous chloride was used with 4 ml of 12N sulfuric acid or 12N perchloric acid.

Table 1. The relations between absorbance and hydrochloric acid concentration.

Concentration of HCl (N)	Absorbance		Observation time after mixed (Min)
5.0	0.310	0.313	40
5.5	0.340	0.342	30
6.0	0.352	0.350	30
6.5	0.342	0.335	30

From the above experiments, it was clarified to be most desirable to determine the small amount of titanium in 6N hydrochloric acid concentration.

5. The amount of sodium alizarinsulfonate

Some experiments were carried out with the various amounts of A. S. solution, by using 20.1 γ of titanium 6N of hydrochloric acid concentration and under the same condition as described above. The results obtained are shown in Table 2, and the estimation of their absorbances was done after standing the solutions for 30 minutes. The absorbance became constant with 0.6 ml of the A. S. solution or more, and so 0.7 ml of the A. S. solution was used in the following experiments.

Table 2. The relation between absorbance and amount of the sodium alizarinsulfonate (A. S.) solution.

A. S. solution (ml)	Absorbance	
0.3	0.270	0.281
0.4	0.302	0.315
0.5	0.330	0.338
0.6	0.352	0.351
0.7	0.352	0.352
0.8	0.352	0.353
0.9	0.350	0.355

6. Amounts of organic salts

20.1 γ of titanium, 0.7 ml of the A. S. solution and 2 ml of the stannous chloride solution were contained in the 10 ml total volume of 6N hydrochloric acid solution, varing the amount of the ammonium oxalate solution, and its absorbance was measured. The results are shown in Table 3. The absorbance became constant with the addition of more than 2.0 ml of the solution, so 2.0 ml of the ammonium oxalate solution was used in the following experiments. The reaction proceeded similarly without the ammonium oxalate solution, but the absorbance was somewhat small.

Table 3. The relation between absorbance and amount of oxalic acid.

Ammonium oxalate solution (ml)	Absorbance	
0	0.332	0.330
0.5	0.341	0.342
1.0	0.340	0.350
1.5	0.354	0.351
2.0	0.359	0.363
2.5	0.359	0.362

Ammonium tartrate, ammonium citrate or ammonium succinate was used intead of ammonium oxalate and the same results as in the case of oxalate were obtained by the addition of 2 ml or more of the ammonum tartrate solution (10 per cent) or the amimonium citrate solution (10 per cent) and 1.5 ml or more of the ammonium succinate solution (5 per cent). Therefore, these salts can be used in the same way.

7. The amount of stannous chloride

Varing the amount of stannous chloride in the 10 ml of 6N hydrochloric acid solution, to which 20.1 γ of titanium, 2 ml of the ammonium oxalate solution and 0.7 ml of the A. S. solution were added, and the absorbance was measured. The results are shown in Table 4. As seen in the results, the suitable amount of stannous chloride solution was 2 ml and it was used in all experiments.

Table 4. The relation between absorbance and amount of stannous chloride.

Stannous chloride (ml)	Absorbance	
1.0	0.326	0.327
1.5	0.349	0.340
2.0	0.360	0.355
2.5	0.352	0.360

8. The relations between the amount of titanium and its absorbance

In the 10 ml of 6N hydrochloric acid solution containing 2 ml of the ammonium oxalate solution, 0.7 ml of the A. S. solution and 2 ml of the stannous chloride solution, the amount of titanium added was changed, and after 30 minutes standing, its absorbance was observed at the wave length 760 mμ. The relation between the amount of titanium and the absorbance was linear with 35 γ or less of titanium in 10 ml of the solution, and with the more titanium the relation slightly deviated from the linear one as shown in Fig. 3. The molecular absorption coefficient of this solution was 8370 at 760 mμ.

9. Procedure of the determination of titanium

The following procedure was proposed according to the above preliminary experiments:

Take the sample solution of titanium (if the volume of the solution is too

much, adjust the volume to about 1 ml by evaporation, or evaporate the solution just to dryness) and dissolve it with 4 ml of hydrochloric acid, adding 2 ml of the ammonium oxalate, 0.7 ml of the A. S. solution and 2 ml of the stannous chloride solution. Dilute this mixture to 10 ml with water and after complete mixing, allow to stand the solution for 30 minutes at the constant temperature 15~20°C and measure the absorbance of the solution at the wave length 760 mμ. The amount of titanium was determined by using the calibration curve in Fig. 3 prepared before.

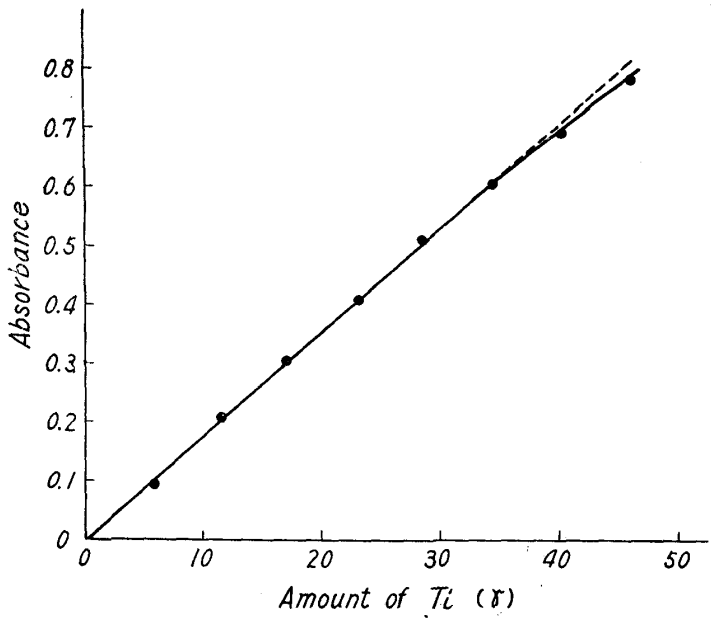

Fig. 3. Calibration Curve.

10. Effects of diverse ions

Various metal ions were added to the 10 ml of 6N hydrochloric acid solution containing 22.9 γ of titanium, 2 ml of the ammonium oxalate solution, 0.7 ml of the A. S. solution and 2 ml of the stannous chloride solution, and its absorbance was observed at 760 mμ. No effect on the determination of titanium was seen by adding such an amount of metal ions as shown in Table 5. It was found that with the addition of about 300 mg of ferric iron, it was necessary to increase a little more amount of stannous chloride, and the maximum absorbance of it developed after 45 minutes or more.

Table 5. The amount of other metallic ions which do not affect the reaction in these amount.

Elements added (used salt)	Amount
Cu (sulphate), Mn (sulphate),	200 γ
Co (sulphate), Ni (sulphate),	〃
Cr (sulphate), Mg (sulphate),	〃
Mo (molybdate), W (tungstate),	〃
V (vanadate), Zr (sulphate),	〃
Ge (sodium hydroxide solution of germanium oxide),	〃
Nb (oxalate complexed salt),	〃
Ta (oxalate complexed salt)	〃
Al (sulphate),	100 mg
Zn (sulphate)	〃
Fe^{2+} (sulphate),	300 mg
Fe^{3+} (sulphate)	〃

III. Discussion on the reaction

Szarvas et al.[4] reported that in this reaction sodium alizarinsulfonate was reduced in the hydrochloric acid solution by hydrogen of nascent state with a catalytic action of titanium and the color turned to green, and that the reaction was, therefore, the catalystic one. In the method established by the present authors, sodium alizarinsulfonate was in the same way and stannous chloride was used as a reducing reagent in the hydrochloric acid solution from the above experiments, and this reaction was applicable for the photometric determination of titanium.

The following experiments were carried out to clarify the mechanism of the reaction. After the addition of the A. S. solution into the hydrochloric acid solution, titanium was also added in the titanous state reduced with liquid zinc amalgam. As soon as titanous solution was added, the color of the solution turned to green, then gradually showed the decoloration, and at last the color returned to yellow. The fact mentioned above shows that titanous ion turned at once to green by the A. S. solution. The present authors considered that titanium was not generally reduced by stannous chloride and that the complex compounds of titanium ion and alizarinsulfonate would be reduced. The following experiment was carried out to prove above consideration:

25.2 γ of titanium was taken and 4 ml of 12N hydrochloric acid, 2 ml of ammonium oxalate and 2 ml of stannous chloride were mixed and total volume was adjusted to be exactly 9.3 ml. After standing the solution for 30 minutes, 0.7 ml of the A. S. solution was added to the solution and mixed well. At every 5 minutes after the addition of A. S. solution, the solution was observed spectrophotometrically. The details of the results were not shown here but the completely same values were obtained as in the case in which the A. S. solution and the stannous chloride solution were added at the same time, and no difference was observed owing to the time of the addition of stannous chloride to titanium. This fact clearly shows that 30 minutes of standing before the addition of the A. S. solution did not help the reduction of titanium at all. It is reasonable to think that the reaction begins only after the addition of the A. S. solution, and that the stannous chloride does not react without the co-existence of titanium and A. S.

This result proves doubtlessly that at first, titanium and A. S. form a complex compound and that this complex compound is reduced by stnnous chloride and its color turns to green.

Summary

1. It was found that when sodium alizarinsulfonate and stannous chloride were added to the hydrochloric acid solution, the color of the solution turned to green by the presence of titanium, and so this reaction was applicable to the determination of titanium by the photometric method.

2. The necessary fundamental experiments were carried out by the spectrophotometer to obtain the suitable conditions for the determination of titanium.
3. The maximum absorbance was in the range from 740 mμ to 790 mμ, and the time required for the development of the maximum coloration depended upon the concentration of hydrochloric acid, and the concentration of 6N hydrochloric acid was most suitable. The suitable amount of sodium alizarinsulfonate, stannous chloride and other reagents were determined.
4. The relation between the absorbance and the amount of titanium was linear.
5. The diverse ions which were present usually did not affect the reaction, if the amount was not so great.
6. The mechanism of this reaction was discused, and it was recognized that the complex compound of sodium alizarinsulfonate and titanium of tetravalent was reduced and shown the coloration.